



## SUBSTITUTE SPECIFICATION

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### LIGHT-EMITTING MATERIAL AND METHOD OF PRODUCING A LIGHT EMITTING MATERIAL HAVING A PARAGENESIS CRYSTALLINE STRUCTURE

#### TECHNICAL FIELD

The present invention relates to a light-emitting material and method producing a light emitting material having a paragenesis crystalline structure, and more particularly, to an inorganic light-emitting material having a long afterglow time using a rare-earth element as an exciting agent and to a method of producing a light emitting material having paragenesis crystalline structure with different phases.

#### BACKGROUND OF THE INVENTION

Light-emitting materials are conventionally mixed in ink or paint to make light emitting paint, to form safety signs, clock boards and the like. Conventionally, copper-excited zinc sulfide (ZnS:Cu) was used as the light-emitting material. ZnS:Cu has high light-emitting efficiency in the light-emitting spectral region, but its brightness decays extremely rapidly, and the visible afterglow time is as short as 20 to 30 minutes. When the ZnS:Cu is exposed to ultraviolet rays in moisture environment, the material will decompose and degenerate rapidly and the body color of the material will darken. For the above reasons, the use of ZnS:Cu is very limited, particularly when used outdoors. A material which can substitute for ZnS:Cu had long been desired.

A light-emitting material having the general formula  $[m(\text{Sr}_{1-x}\text{Eu}_x)\text{O} \cdot n\text{Al}_2\text{O}_3 \cdot y\text{B}_2\text{O}_3]$  is known and disclosed in CN1053807A. In this formula m,

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n, x, and y represents:  $1 \leq m \leq 5, 1 \leq n \leq 8, 0.005 \leq y \leq 0.35$  and  $0.001 \leq x \leq 0.1$ . The afterglow time of this light-emitting material is in a range of from 10 to 20 hours.

USP 5,376,303, teaches the use of phosphor having long afterglow ability in a compound comprising  $(MO \cdot a (Al_{1-b}B_b)_2O_3 : cR)$ , wherein a, b and c are defined as:  $0.5 \leq a \leq 10.0, 0.0001 \leq b \leq 0.5, 0.0001 \leq c \leq 0.2$  and wherein MO is at least one compound selected from a group consisting of MgO, CaO, SrO and ZuO. and R consists of Eu and at least one additive rare-earth element selected from a group consisting of Pr, Nd, Dy and Tm.

In the above-mentioned patent, some phosphors such as  $SrO \cdot 2.10(Al_{10.952}B_{0.048})_2O_3 : 0.005Eu, 0.020Dy$  (which will be referred to as "A" hereinafter), and  $SrO \cdot 1.025(Al_{0.976}B_{0.024})_2O_3 : 0.005Eu, 0.015Dy$  (which will be referred to as "B" hereinafter) were disclosed. The residual light-emitting time and brightness of these phosphors were evaluated to find out the afterglow time constant (n) and relative brightness as compared to ZnS:Cu, Cl. The test results established afterglow time constants for the A and B phosphors and for ZnS:Cu, Cl to be 0.94, 0.86 and 1.26, respectively, and the phosphorus brightness after 10 seconds to be 144, 220 and 100, respectively. Moreover, the phosphorus brightness after 20 seconds was 934, 1320 and 100, respectively. The afterglow time and brightness for these A and B phosphors are clearly improved relative to ZnS:Cu, Cl, but they are not yet in practical use.

## SUMMARY OF THE INVENTION

The present inventors conducted research for producing light-emitting material using the rare-earth element Eu as the light-emitting material and discovered that a light-emitting material having a new crystallization structure was

obtained by adding an appropriated amount of B and an additive exciting agent Dy. This light-emitting material has a very desirable long afterglow time and high brightness.

The light-emitting material of the present invention is a new compound that has a paragenesis crystalline structure consisting of two different phases expressed in a general formula:  $(\text{Sr, Eu, Dy})_{0.95 \pm X}(\text{Al, B})_2\text{O}_{3.95 \pm X} \cdot (\text{Sr, Eu, Dy})_{4-X}(\text{Al, B})_{14}\text{O}_{25-X}$  ( $X=0.01 \sim 0.1$ ).

This new compound has a crystallization structure which consists of two phases, i.e.,  $(\text{Sr, Eu, Dy})_{0.95 \pm X}(\text{Al, B})_2\text{O}_{3.95 \pm X}$  and  $(\text{Sr, Eu, Dy})_{4-X}(\text{Al, B})_{14}\text{O}_{25-X}$  respectively. This conclusion was obtained from XRD (X-ray diffraction) analysis using a large amount of samples carried out in the Chemical Laboratory of Crystallization Structure and Crystallization which is a material scientific division of the Chinese Geological University in China. Based on the XRD analysis, and using an optical microscope and electronic probe analytical technique, it was corroborated that the above two phases are paragenesis and both of them have light-emitting function.

The method of producing a light-emitting material in accordance with the present invention comprises the step of:

- (1) pulverizing raw material(s) selected from the group consisting of:  $\text{SrCO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{Eu}_2\text{O}_3$  and  $\text{Dy}_2\text{O}_3$ ;
- (2) heating the pulverized raw material(s) at a temperature in a range of between  $850^\circ\text{C}$  to  $1200^\circ\text{C}$  for three hours under a reduction condition;
- (3) maintaining the temperature relatively constant and substantially equal to  $1200^\circ\text{C}$  to form a sintered body;
- (4) cooling the sintered body down to room temperature, and

(5) pulverizing the sintered body.

In the heating step, the temperature should preferably be maintained constant at about 1200°C for 5-6 hours.

#### BEST MODE FOR CARRYING OUT THE INVENTION

The light-emitting material of the present invention was assessed using analytical means such as X-ray fluorescent analysis, plasma spectral analysis, electronic probe and X-ray photoelectron energy spectrum to confirm that the content of the element B in the new compound was between 0.2~1.0% by weight and that the contents of the elements Eu and Dy were present in a range of between 0.5 to 3.0% by weight and 0.01 to 3.0% by weight, respectively.

The element B exists in the entire crystallization structure. Moreover, the element B exists in a form of B-O tetrahedral coordination or  $\text{BO}_3$  triangular coordination. The  $\text{BO}_3$  triangular coordination can substitute a portion of Al-O octahedron. This causes instability in the crystallization structure and is an important structural feature of the light-emitting material of the present invention.

Further, the Al-O octahedron and Al-O tetrahedron concurrently exist in the new compound crystallization of the present invention, and form a substantially hexagonal ring with positive ions of Sr, Eu and Dy charged into a cavity of the ring. It is believed that from an ion balance consideration that the content of Al is slightly excessive and that the amount of the elements (Sr, Eu, Dy) is less and somewhat insufficient.

The raw materials which are used for the producing method of the light-emitting material of the present invention are  $\text{SrCO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{Eu}_2\text{O}_3$ , and  $\text{Dy}_2\text{O}_3$ , of which,  $\text{Eu}^{3+}$  of  $\text{Eu}_2\text{O}_3$  is reduced to  $\text{Eu}^{2+}$  during the sintering process to

excite the new compound and cause light-emitting function.  $\text{Dy}_2\text{O}_3$  strengthens the exciting effect of  $\text{Eu}_2\text{O}_3$  as an additive exciting agent.

The term "reduction to  $\text{Eu}^{2+}$ " as used in the present invention means to reduce the above-mentioned mixed raw materials using carbon power, or to reduce the mixed raw material using a gas mixture of nitrogen and hydrogen at a volume ratio of 4:1.

The light-emitting material produced by the invention has faint yellow-green color. When this light-emitting material is irradiated with sunlight, a fluorescent light or the other artificial light source and excited, the main peak of the light-emitting spectrum is 505nm, and shows greenish blue.

As a result of measurement of samples, it was found that the light-emitting material of the present invention showed brightness of about  $8500\text{mcd/m}^2$  after five seconds from the instant that the irradiation was stopped and has a visible afterglow time of 80 hours or longer (see Table 1). As shown in Table 1, the light-emitting material produced by the method of the present invention has especially excellent visible afterglow time.

The brightness is measured by the following method. That is, 0.2g of sample is put in a plastic plate of 10mm diameter and it is irradiated with a fluorescent light of 15w for 15 minutes from a perpendicular distance of 20cm at a room temperature and under humidity of 25RH%, and brightness of each sample is measured at various time points using an luminance meter (TOPCON BM-5, Japan TOPCON Inc.)

The light-emitting material produced by the method of the present invention has apparently long afterglow time in comparison with similar other products. Therefore, this material can suitably be applied to articles or safe sign which need

to be seen in the dark, for example, a fireplug of a fire extinguishing tools and material, a handrail of safe stairs, and a road.

The following are examples of the present invention.

#### EXAMPLE I

Previously pulverized 372.89g of  $\text{SrCO}_3$ , 220.32g of  $\text{Al}_2\text{O}_3$ , 12.616g of  $\text{H}_3\text{BO}_3$ , 2.42g of  $\text{Eu}_2\text{O}_3$ , and 0.157g of  $\text{Dy}_2\text{O}_3$ , were measured and sufficiently mixed.

The mixed raw material was put into a container and it was covered with carbon powder, and heated at a temperature in a range of between  $850^\circ\text{C}$  to  $1200^\circ\text{C}$  for three hours to raise its temperature, and the temperature was then maintained constant for six hours at  $1200^\circ\text{C}$ . Then, the mixture was naturally cooled down to room temperature to form a sintered body. The sintered body was pulverized into such small powders that all the powders could pass through 200 mesh, thereby forming the product.

The product obtained in this manner had initial brightness of  $3850\text{mcd/m}^2$  for 30 seconds and afterglow time was 85 hours.

In the obtained produce, a value of X in the general formula was 0.01.

#### EXAMPLE II

Previously pulverized 409.76g of  $\text{SrCO}_3$ , 220.32g of  $\text{Al}_2\text{O}_3$ , 12.616g of  $\text{H}_3\text{BO}_3$ , 2.96g of  $\text{Eu}_2\text{O}_3$ , and 0.164g of  $\text{Dy}_2\text{O}_3$ , were measured and sufficiently mixed.

The mixed raw material was put into a container and it was covered with carbon powder, and heated at a temperature of between  $850^\circ\text{C}$  to  $1000^\circ\text{C}$  for three hours to raise its temperature, and the temperature was maintained for six hours at  $1000^\circ$ . Then, the mixture was naturally cooled down to room temperature

to form a sintered body. The obtained sintered body was pulverized into such small powders that all the powders could pass through 200 mesh, thereby obtaining a product.

The product obtained in this manner had initial brightness of 3990 mcd/m<sup>2</sup> for 30 seconds and the afterglow time was 80 hours for the obtained product the value of X in the general formula was 0.01.

Table 1

Measurement of brightness ( $\text{mcd/m}^2$ ) and calculation of standard deviation

Time	Sample No.					Calculation of standard deviation		
	1	2	3	4	5	Average value	Standard deviation	Relative standard deviation
5 s	8400	8450	8400	8500	8500	8430	45	0.5%
10 s	7380	7570	7420	7410	7320	7460	125	1.8%
20 s	5120	5130	4930	5170	4870	5044	135	2.7%
30 s	4030	3960	3850	3990	3820	3930	91	2.3%
40 s	3380	3230	3160	3310	3110	3238	110	3.4%
60 s	2550	2490	2430	2490	2420	2476	53	2.1%
90 s	1870	1820	1780	1830	1750	1810	47	2.6%
3min	1520	1470	1460	1480	1420	1470	36	2.4%
4 min	870	850	840	840	820	844	18	2.1%
5 min	760	740	720	730	700	730	22	3.0%
3 min	630	630	610	610	590	614	17	2.8%
15 min	330	310	300	310	290	308	15	4.9%
30 min	160	150	140	140	130	144	15	8.3%
60 min	70	70	60	60	60	64	5.5	8.6%
90 min	50	40	40	50	40	44	5.5	12.5%
120 min	40	40	30	40	30	36	5.5	15.3%
180 min	20	30	20	20	20	22	4.5	20.5%
240 min	20	20	10	20	20	18	4.5	25.0%
360 min	20	10	10	20	10	14	5.5	33.6%
480 min	10	10	10	10	10	10	0	0